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Palladium-complex-catalyzed regioselective Markovnikov addition reaction and dehydrogenative double phosphinylation to terminal alkynes with diphenylphosphine oxide

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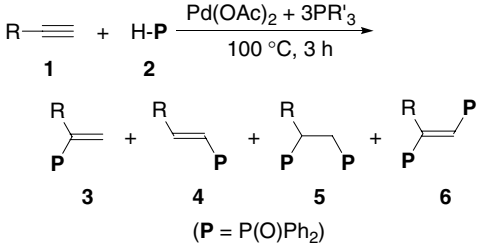
Abstract—Palladium-1,2-bis(diphenylphosphino)ethane complex catalyzes regioselective Markovnikov addition of diphenylphosphine oxide to terminal alkynes in propionitrile, while the use of triarylphopshines, di(*o*-tolyl)phenylphosphine in particular, as the ligand leads to dehydrogenative double addition forming 1,2-diphenylphosphinyl-1-alkenes as major products.

α,β-Unsaturated organophosphorus(V) compounds[1] are a useful class of intermediates that undergo myriad synthetic organic transformation reactions. They are also valuable as flame retardants, precursors therefore and monomers for flame retardant polymers.[2] 1,2-Phosphinylalkenes that have $R_2P(O)C{=}CP(O)R_2$ linkages are another useful class of phosphorus compounds as intermediates for optically active phosphine ligands,[3] cocatalysts in polymerization of olefins and direct synthesis of organosilanes,[4] extractants for lanthanide and actinide metals.[5] Accordingly, synthesis of these compounds continues to be an active area of research.[6] One of us has also been engaged in metal-catalyzed synthesis of organophosphorus(V) compounds and developed novel addition reactions of hydrogen phosphonates, secondary phosphine oxides, and related compounds with alkynes, alkenes and other unsaturated compounds.[6b,7] A great feature of these reactions lies in the high regioselectivity. For instance, the reaction of hydrogen phosphonate, $H–P(O)(OR)_2$, with terminal alkynes forms branched products when run in the presence of palladium catalysts,[7a] while the same reaction catalyzed by rhodium complexes affords linear products.[7d] On the other hand, the monodentate phosphine–palladium complex-catalyzed reaction of diphenylphosphine oxide, $H–P(O)Ph_2$, with terminal alkynes forms linear products.[7b] To switch the regioselectivity in this reaction, addition of acidic compounds like diphenylphosphinic acid has proven to be a powerful tool.[7c] However, the use of acidic additives can be a serious drawback for commercial implementation. This communication discloses highly branch-selective addition of diphenylphosphine oxide by using 1,2-bis(diphenylphosphino)ethane (dppe) as ligand without addition of acidic additives (Scheme 1). Preliminary results of dehydrogenative double phosphinylation of terminal alkynes affording 1,2-bis(diphenylphosphinyl)alkenes (**6**),[8] which was accidentally found, are also briefly reported.

Ligand screening experiments using palladium acetate and a series of phosphine ligands[9] (P/Pd = 3) have revealed that chelating phosphines afford branched



Scheme 1.

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adduct **3** as a major product. For instance, the reaction of $HP(O)Ph_2$ (**2**) with *p*-tolylacetylene (**1a,** 1.05 equiv) run in toluene at 100 °C for 3 h in the presence of dppe formed **3a** in 63% NMR yield, together with **4a** (2%), **5a** (9%),[10] and **6a** (4%),[11] the branch-selectivity among single-addition products [$= 100 \times \mathbf{3a}/(\mathbf{3a} + \mathbf{4a})$] being 97%. 1,3-Bis(diphenylphosphino)propane (branch-selectivity = 94%), 1,4-bis(diphenylphosphino)butane (96%), and *o*-bis(diphenylphosphino)benzene (93%) behaved similarly to dppe while 1,2-bis(9-phosphafluoren-9-yl)ethane (71%) and 1,1′-bis(diphenylphosphino)ferrocene (81%) were inferior. Use of $Pd(PPh_3)_4$ did not furnish high selectivity under the same conditions, ending up with the formation of **3a**, **4a**, **5a**, and **6a** in 26%, 30%, 6%, and 4% yields, respectively.[11,12]

Nature of solvents appears to affect the yield of the branched product. In the reaction of 1-octyne (**1f**) under the same conditions using the $Pd(OAc)_2$–dppe catalyst system, the yield of the branched product (**3f**) decreased in the following order; propionitrile (81% ^1H NMR yield based on the quantity of **2** charged) > 4-methyl-2-pentanone (77%) > chlorobenzene (74%) > 1,4-dioxane (68%) = toluene (68%) > dimethylformamide (64%) > *n*-octane (9%) > ethanol (6%).[13] In all these reactions the formation of the corresponding linear product (**4f**) was ⩽1% and the branch-selectivity was ⩾ 98% except for the reactions in octane (83%) and ethanol (86%). The same trend was also observed in the reaction of **1a**. These experiments suggest that propionitrile is the solvent of choice.

As summarized in Table 1, the new procedure works well with other terminal alkynes.[14] No significant difference in reactivity was evident between aliphatic and aromatic alkynes. In most of these reactions, the branch-selectivity was higher than 90% and only traces (<1% yield) of compounds **5** and **6** were occasionally formed. However, as was observed in the addition of hydrogen phosphonate with terminal alkynes,[7a] trimethylsilylacetylene was an exceptional alkyne to furnish the corresponding linear product in a low yield.[15] In the $Pd(PPh_3)_4$-catalyzed hydrophosphinylation of terminal alkynes with diphenylphosphine oxide, which normally furnished linear products, 1-ethynylcyclohexene was an exceptional alkyne to afford a branched product.[7b] In the present reaction, however, this particular alkyne did not show an exceptional behavior.

Table 1. Pd–dppe-catalyzed selective Markovnikov addition of diphenylphosphine oxide[a]

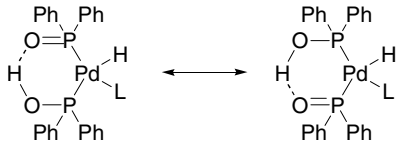
Entry	R—C≡CH	Yield[b] (%)		Selec[c] (%)
	1, R =	**3**	**4**	
1	**1a**, *p*-$CH_3C_6H_4$	**3a** 88 (83)	**4a** 2	98
2	**1b**, C_6H_5	**3b** 77	**4b** 4	95
3	**1c**, *p*-FC_6H_4	**3c** 67 (59)	**4c** ~0	>99
4	**1d**, 2-Thienyl	**3d** 56 (51)	**4d** ~0	>99
5	**1e**, Ferrocenyl	**3e**—(78)	**4e**—(2)	98
6	**1f**, *n*-C_6H_{13}	**3f** 81	**4f** 1	99
7[d]	**1g**, *t*-Bu	**3g** 76 (70)	**4g** 2	97
8	**1h**, 1-Cyclohexenyl	**3h** 64	**4h** 7	90
9	**1i**, $MeOOC(CH_2)_3$	**3i** 74 (42)	**4i** ~0	>99
10	**1j**, $HO(CH_2)_4$	**3j** 72 (69)	**4j** ~0	>99
11	**1k**, $(CH_3)_3Si$	**3k** 0	**4k** 10	0

[a] Reactions were performed using alkyne **1** (1.39 mmol), diphenylphosphine oxide **2** (1.33 mmol), $Pd(OAc)_2$ (5 mol %) and dppe (1.5 equiv relative to $Pd(OAc)_2$ in 5 mL propionitrile at 100 °C for 3 h).

[b] Determined by ^1H NMR spectroscopy or gas chromatography and based on **2** charged. The figure in parentheses is isolated yield.

[c] $100 \times \mathbf{3}/(\mathbf{3} + \mathbf{4})$.

[d] Reaction time = 5 h.



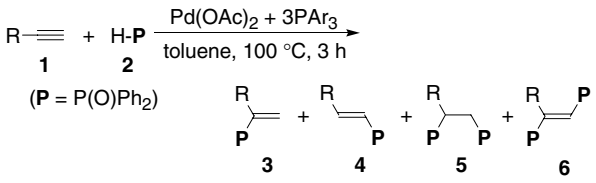
Scheme 2. Species **7** (L = monodentate phosphine).

The provenance of the branch-directing nature of dppe is ambiguous at this stage. The monodentate phosphine–palladium complex-catalyzed reaction has been proposed to proceed through species **7** (Scheme 2) as an active species, which has a six-membered ring, formed by intramolecular hydrogen bonding.[16,7b] In the present reaction catalyzed by the palladium–dppe catalyst system, generation of the six-membered intermediate, which is responsible for the linear product formation, is envisioned to be hampered by strong chelation of dppe. Although further detailed explanation is premature, the branch-selectivity is presumably associated with the lack or difficulty of the generation of such a six-membered intermediate.

As already mentioned, another very interesting observation in the foregoing reaction of *p*-tolylacetylene (**1a**) run in toluene is the formation of compound **6a**. Surprisingly **6a** has an (*E*)-geometry, which was suggested by NMR spectroscopy and was confirmed by comparison with an authentic sample synthesized via a different route.[8] Although detailed study on the effect of ligands, solvents and the operating conditions is in progress, preliminary screening of ligands has revealed that a triarylphosphine, di(*o*-tolyl)phenylphosphine in particular, is better performing than dppe in terms of the selectivity for **6a** (24% yield[11] with $P(o\text{-Tol})_2Ph$ vs 4%[11] with dppe under the conditions of typical procedure[14]). By using 2 equiv of **2** (relative to **1**), we were able to obtain dehydrogenative double phosphinylated products as major products (Table 2). Addition of hydrogen acceptors like methyl acrylate and diethyl vinylphosphonate was occasionally beneficial to enhance the formation of **6**, presumably associated with hydrogen generation during its formation.

The mechanism of (*E*)-**6** formation merits further consideration. Initial formation of (*Z*)-**6** followed by isomerization to (*E*)-**6** can be safely ruled out since separately prepared (*Z*)-**6a**[17] did not isomerize when exposed to the catalytic reaction conditions. An alternative route to (*E*)-**6** may stem from intermediate formation of alkynylphosphine oxide,[18] which reacts further with a second molecule of **2**. However, this possibility is not

Table 2. Reaction of diphenylphosphine oxide with terminal alkynes in the presence of Pd–PAr_3 catalysts[a]



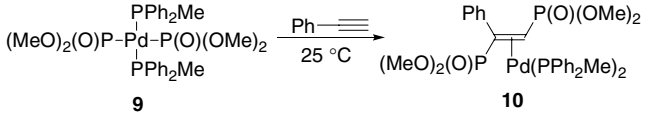
R—C≡CH	PAr_3	Yield[b] (%)			
1, R=		**3**	**4**	**5**	**6**
1b, *p*-Tolyl[c]	$P(o\text{-Tol})_2Ph$	1	5	2	34
1d, 2-Thienyl[d]	$P(o\text{-Tol})_2Ph$	~0	~0	9	48
1f, *n*-Hexyl	PPh_3	3	2	nd[e]	14

[a] Reactions were performed using alkyne **1** (0.695 mmol), diphenylphosphine oxide **2** (1.39 mmol), $Pd(OAc)_2$ (5 mol %), and PAr_3 (3.0 equiv relative to $Pd(OAc)_2$) in 2.5 mL toluene at 100 °C for 3 h.
[b] Determined by NMR spectroscopy and based on the quantity of **1** charged.
[c] Run in the presence of ethyl vinylphosphonate (1.0 equiv relative to **1b**).
[d] Methyl acrylate (1.0 equiv relative to **1d**) was added.
[e] Not determined.

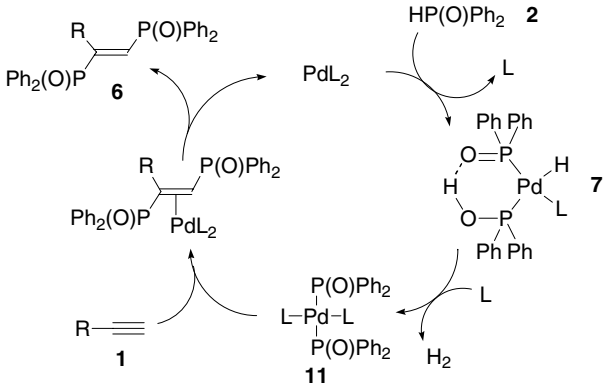
likely either in view of the following experiments. Thus, separately prepared (*p*-tolylethynyl)diphenylphosphine oxide (**8**)[19] reacted with **2** in the presence of the $Pd(OAc)_2$–$3PPh_3$ catalyst system at 100 °C for 3 h to afford 61% yield of a mixture of (*E*)-**6a** and (*Z*)-**6a** in a 32:68 ratio. The ratio did not change at all when the reaction time was prolonged to 9 h, which also suggests the lack of the isomerization of (*Z*)-**6a** to (*E*)-**6a**. Furthermore, uncatalyzed reaction of **8** with **2** under the same conditions also afforded a mixture of (*E*)-**6a** and (*Z*)-**6a** in a 43:57 ratio (41% total yield).

In the mechanistic study on hydrophosphorylation of alkynes with hydrogen phosphonates, *cis*-$Me_2Pd(PPh_2Me)_2$ was treated with $HP(O)(OMe)_2$ at 25 °C overnight to generate *trans*-$Pd[P(O)(OMe)_2]_2(PPh_2Me)_2$ (**9**).[7a] Upon treatment with phenylacetylene (1 equiv), complex **9** was transformed to palladium(0) species (**10**) ligated by (*E*)-phenyl-1,2-bis(dimethoxylphosphinyl)ethene, as near a sole product (Scheme 3), which could be liberated by exposure to air.[20]

It is interesting to note the consistency of the configuration of the double bond in complex **10** and that of **6** formed in the present catalytic reaction. Although the monodentate phosphine–palladium-catalyzed addition of $HP(O)Ph_2$ under milder conditions is carried by species **7**, it may be possible, depending on the conditions and the nature of the ligand, that $Pd[P(O)Ph_2]_2L_2$ (**11**), analogous to **9**, is generated, somehow leading to the formation of **6** (Scheme 4). The formation of (*E*)-**6** (and also of (*E*)-**10**) is somewhat unusual if we assume cis-insertion followed by reductive elimination. However, trans-insertion is not totally impossible, in view of precedents.[21,22]



Scheme 3.



Scheme 4.

In summary, this Letter clearly demonstrates the key roles of the ligand played in the reaction of terminal alkynes with diphenylphosphine oxide. Optimization of the dehydrogenative double phosphinylation and mechanistic aspects of the addition of diphenylphosphine oxide will be reported shortly.

Acknowledgments

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8. Quite recently Oshima and co-workers reported an elegant radical reaction involving chlorodiphenylphosphine, diphenylphosphine, triethylamine, and a terminal alkyne leading to a 1,2-bis(diphenylphosphino)alkene, which could be readily oxidized with hydrogen peroxide to furnish a 1,2-bis(diphenylphosphinyl)alkene. See: Sato, A.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2005**, *44*, 1694.
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11. In view of possible oligomerization of **1a**, we used a slight excess of **1a**. For clearer understanding of the reaction profile forming both single and double phosphinylated products (**3a**, **4a**, **5a**, and **6a**), however, the product yields in this particular reaction were tentatively calculated based on the quantity of **1a** charged.
12. The higher branch-selectivity in this experiment (100 °C), as compared with the branch-selectivity (<5%) observed at 70 °C suggests that the higher reaction temperature is also a factor that enhances the branch-selectivity. See Ref. 7b.
13. Conversions of diphenylphosphine oxide in the reactions run in *n*-octane and ethanol were only 40% and 18%, respectively.
14. *Typical procedure:* A mixture of $Pd(OAc)_2$ (0.067 mmol), dppe (0.10 mmol), diphenylphosphine oxide (1.33 mmol), and *p*-tolylacetylene (1.39 mmol) dissolved in propionitrile (5 mL) was heated at 100 °C for 3 h. The resulting mixture was evaporated and analyzed by ^1H NMR spectroscopy in $CDCl_3$ using *p*-dimethoxybenzene as internal standard. Evaporation of $CDCl_3$ and column chromatography using hexane/ethyl acetate (1/1) afforded **3a** in 83% yield.
15. Despite the low yield of **4k**, **5k**, and **6k** were not formed at all. We thank reviewers who recommended us to examine the reaction of trimethylsilylacetylene, which displayed the exceptional behavior.
16. Secondary phosphine oxides exist in two tautomeric isomers, P(O)H and P(OH), the former being dominant in the equilibrium. See: (a) Bailey, W. J.; Fox, R. B. *J. Org. Chem.* **1963**, *28*, 531; (b) Bailey, W. J.; Fox, R. B. *J. Org. Chem.* **1964**, *29*, 1013; (c) Hamilton, L. A.; Landis, P. S.. In *Organic Phosphorus Compounds*; Kosolapoff, G. M., Maier, L., Eds.; Wiley: New York, 1972; Vol. 4, Chapter 11.
17. Obtained from a mixture resulting from an uncatalyzed reaction of (*p*-tolylethynyl)diphenylphosphine oxide (**8**) with **2** run at 100 °C for 3 h in toluene (vide infra).
18. In the present reaction of *p*-tolylacetylene, we do have detected a trace of (*p*-tolylethynyl)diphenylphosphine oxide.
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